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Ultra-sensitive measurements of ^{233}U by accelerator mass spectrometry for national security applications.

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Abstract

By making modifications to our previously established measurement setup, we increased our abundance sensitivity for ^{233}U by three orders of magnitude and can now measure $^{233}\text{U}/^{238}\text{U}$ ratios as low as 10^{-13} . Because ^{233}U has separate production pathways than ^{236}U , it can provide valuable information on the particular source of anthropogenic uranium in a sample. We demonstrated the utility of our improved capability by using ^{233}U to distinguish separate sources of anthropogenic uranium in a set of samples collected from a contaminated site. In the future, we plan to apply our new capability to characterizing ^{233}U in a wide range of uranium materials.

Introduction

Isotopic signatures are powerful tools for determining the source of nuclear materials in the environment¹. Such signatures often play a critical role in nuclear forensics^{2,3}. One potential isotopic signature is ^{233}U , an anthropogenic isotope of uranium that is present in irradiated nuclear fuel. The two primary production pathways for ^{233}U are: 1) neutron capture on ^{232}Th followed by two successive beta decays; 2) alpha decay of ^{237}Np followed by beta decay of ^{233}Pa . Like ^{236}U , the presence of ^{233}U is an indicator that uranium has been exposed to a neutron environment, but because the production rates for ^{233}U are much lower, it has generally been less exploited as a signature of anthropogenic uranium. However, since the pathways that produce ^{233}U are different than for ^{236}U , it has great potential for not only indicating the presence of anthropogenic uranium in the environment, but also for distinguishing various sources.

Determination of ^{233}U by radiometric methods is difficult because of the long half-life ($t_{1/2} = 159,200$ yr) and the similar alpha-decay energy of ^{234}U (^{233}U : 4.824 MeV; ^{234}U : 4.776 MeV). Traditional mass spectrometry suffers from isobaric interferences from hydride molecules of ^{232}Th , which is difficult to completely remove from a sample, and from tailing effects from ^{234}U . In contrast, accelerator mass spectrometry, which is insensitive to molecular isobars, is capable of precisely quantifying trace amounts (10^3 to 10^5 atoms) of long-lived radionuclides in the presence of an overwhelming abundant isotope (e.g., abundance sensitivity 10^{-13} to 10^{-17})^{4,5}. We have recently completed upgrades to our heavy-isotope AMS system that have enabled us to dramatically increase

our sensitivity and dynamic range for ^{233}U . Here, we describe these developments and demonstrate the utility of ^{233}U as an isotopic signature for anthropogenic uranium.

Experimental

Our heavy-isotope AMS system has been described previously⁶, however recent upgrades to our system have enabled us to improve our measurement scheme for ^{233}U . A brief discussion of these changes follows.

Our previously established protocols for determination of ^{233}U relied on direct measurement of the $^{233}\text{U}/^{236}\text{U}$ ratio. Unlike traditional AMS where the normalizing isotope is measured as a current in a Faraday cup, the typically low levels of ^{233}U and ^{236}U required that both be measured as a count-rate in a gas-ionization chamber detector. This presented a fundamental limit to the mass of uranium (typically $<1\mu\text{g}$, dependent on the $^{236}\text{U}/^{238}\text{U}$ in a particular sample) that could be loaded into our ion source in order to avoid unacceptably high dead-times associated with high count-rates. Based on this level of sample loading and our instrumental background of ^{233}U of 10^5 atoms, our abundance sensitivity for ^{233}U was limited to 10^{-10} relative to ^{238}U .

Recent modifications to our AMS system have enabled us to dramatically improve our measurement scheme for ^{233}U . First, an upgrade to our low-energy injection system more than doubled the amount of beam that we can inject into our tandem accelerator. Second, we reconfigured our high-energy analyzing system to allow current

measurement in a Faraday cup on the high-mass side of the isotope of interest. Both of these modifications enabled us to increase sample loading to ~1 mg of uranium and thereby produce ^{238}U beam currents that could be precisely measured at the high-energy end of our system. Furthermore, since our instrumental background for ^{233}U remained unchanged with this increased sample loading, we achieved a factor of 1000 increase in our abundance sensitivity for ^{233}U . Thus, isotope ratios ($^{233}\text{U}/^{238}\text{U}$) of 10^{-13} and lower can now be measured by our heavy-isotope AMS system.

Results and Discussion

We tested our new measurement scheme for ^{233}U by preparing a series of replicate samples with known additions of a ^{233}U tracer (Isotope Products Laboratories 7233(1172.06)) to samples of well-characterized natural uranium (New Brunswick Laboratory CRM 112-A) and processing these samples by our established chemical protocols. We also included unspiked samples as blanks. The results of the measurement of these samples are shown in Figure 1. The linear fit of our instrumental response versus the intrinsic or expected $^{233}\text{U}/^{238}\text{U}$ ratio is excellent, and the agreement of the triplicate samples at each spike level was within the measurement error which demonstrates the high level of reproducibility of the measurements. The mean value for the six unspiked samples was $^{233}\text{U}/^{238}\text{U} = 7.58 \times 10^{-14}$ which represents an improvement in abundance sensitivity of over three orders of magnitude compared with our previous measurement setup.

To validate our new measurement scheme we performed a cross-comparison on a set of highly-enriched uranium samples that were previously measured by multi-collector inductively-coupled plasma mass spectrometry (MC-ICP-MS). These samples had relatively high $^{233}\text{U}/^{238}\text{U}$ ratios so we performed a quantitative dilution with the NBL CRM 112-A. This dilution was necessary to not only lower the $^{233}\text{U}/^{238}\text{U}$ ratio to avoid dead-time issues with the ^{233}U count rate, but also to increase the $^{238}\text{U}/^{235}\text{U}$ ratio so that 1 mg of material would yield sufficient ^{238}U current for measurement. The results of these measurements are summarized in Table I. The agreement between MC-ICP-MS and AMS is excellent for sample LLNL-1, however only reasonable agreement was achieved for samples LLNL-2 and LLNL-3. Further investigation is needed to determine the reason why the MC-ICP-MS and AMS measurements for these two samples disagree.

Finally, we demonstrated the utility of our new ^{233}U measurement scheme on a set of environmental samples collected from a contaminated site. The bulk uranium extracted from these samples was analyzed by MC-ICP-MS and showed a distinct deviation from natural with respect to the $^{238}\text{U}/^{235}\text{U}$ (Figure 2) ratio which indicates the presence of enriched uranium. However, from the major and minor isotopes alone, one can not conclusively determine whether there may be an additional source of enriched uranium besides the known contamination at the collection site. Due to large measurement errors, a similar deviation was not observable in the $^{234}\text{U}/^{235}\text{U}$ ratio, also measured by MC-ICP-MS. In order to elucidate the nature of the $^{238}\text{U}/^{235}\text{U}$ deviation, we measured the $^{233}\text{U}/^{238}\text{U}$ ratio in these samples by AMS (Figure 3a). The samples clearly fall on a double-isotope mixing line when $^{233}\text{U}/^{238}\text{U}$ is plotted against $^{238}\text{U}/^{235}\text{U}$.

However, we also measured a field control sample (shown on the expanded scale in Figure 3b) from the same site and this “field blank” is significantly shifted from the mixing line of the samples. This indicates that while there is anthropogenic uranium present at this site, the source is clearly distinct from the uranium in the samples. These results demonstrate the utility of our low-level ^{233}U measurement capability to identify distinct sources of anthropogenic uranium.

Conclusions and Future Work

We have successfully developed an improved measurement capability for ^{233}U by AMS. This capability can measure $^{233}\text{U}/^{238}\text{U}$ ratios as low as 10^{-13} , which represents a factor of a thousand improvement over our previous setup. We performed a cross-comparison by measuring a set of highly-enriched uranium samples by MC-ICP-MS and AMS and obtained excellent agreement for one of the samples. However, for the other two comparison samples, there was a distinct positive bias with the MC-ICP-MS data compared to the AMS results. Further investigation is required to explain the cause of this bias. We demonstrated the utility of our improved capability by measuring $^{233}\text{U}/^{238}\text{U}$ in a set of uranium samples collected from a site known to be contaminated with anthropogenic uranium. The ^{233}U results show the presence of a source of anthropogenic uranium that is clearly distinguished from the residual contamination from the site. Based on this demonstration of the utility of ^{233}U AMS, we are planning to apply our new capability to characterizing the ^{233}U content in a wide range of uranium sources.

Acknowledgements

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Tables

Table I. Results of the cross-comparison between MC-ICP-MS and AMS for the measurement of $^{233}\text{U}/^{238}\text{U}$ in a set of highly-enriched uranium samples.

Sample ID	ICP-MS ($\times 10^{-6}$)		AMS ($\times 10^{-6}$)	
	$^{233}\text{U}/^{238}\text{U}$	2- σ	$^{233}\text{U}/^{238}\text{U}$	2- σ
LLNL-1	4.796	0.082	4.803	0.120
LLNL-2	7.031	0.095	6.495	0.065
LLNL-3	7.012	0.084	6.295	0.061

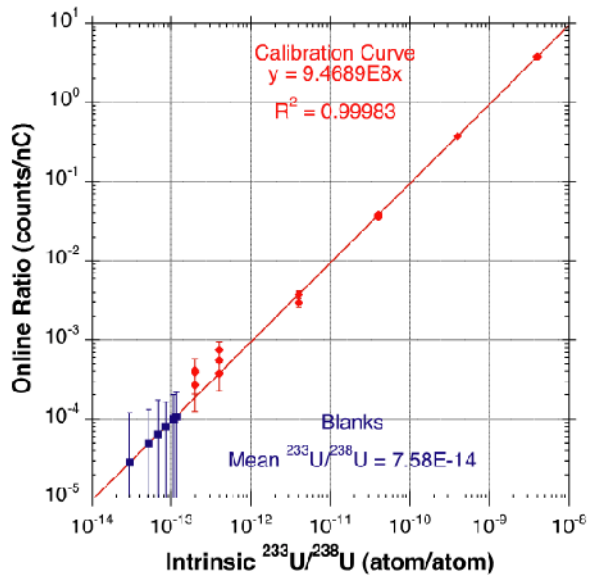
Figure Captions

Figure 1. A calibration curve from the measurement of a series of standards (diamonds) and blanks (squares). The standards were prepared by quantitatively mixing ^{233}U tracer solution (Isotope Products Laboratories 7233(1172.06)) with a source of natural uranium (New Brunswick Laboratory CRM 112-A), which was treated as a blank. Each standard was analyzed in triplicate.

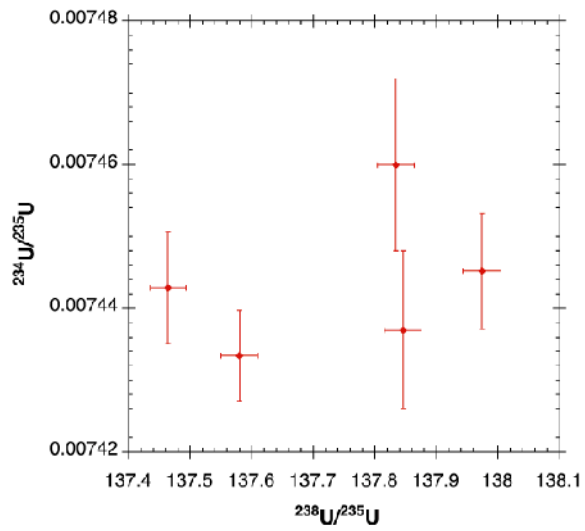
Figure 2. Two-dimensional isotope ratio plot of the major ($^{238}\text{U}/^{235}\text{U}$) and minor ($^{234}\text{U}/^{235}\text{U}$) isotopes of uranium measured for a set of environmental samples collected from a contaminated site. These data were obtained by multi-collector ICP-MS.

Figure 3. Two-dimensional isotope ratio plots of the major ($^{238}\text{U}/^{235}\text{U}$) and trace ($^{233}\text{U}/^{238}\text{U}$) isotopes of uranium measured for a set of environmental samples collected from a contaminated site. Plot 3a shows the double-isotope mixing line for the samples, while plot 3b shows the same mixing line on an expanded scale to show the field blank. The $^{233}\text{U}/^{238}\text{U}$ data were obtained by AMS, and the $^{238}\text{U}/^{235}\text{U}$ data were obtained by multi-collector ICP-MS.

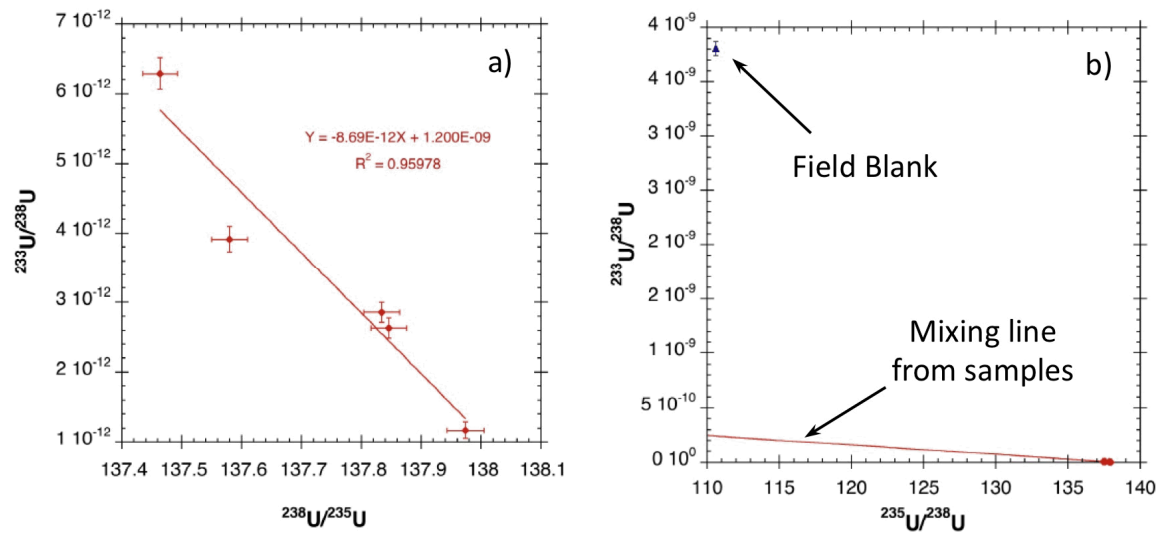
Figures



Log 375 – Tumey – Figure 1



Log 375 – Tumey – Figure 2



Log 375 – Tumey – Figure 3